Diversity of morphological patterns in supramolecular polymers formed from the amphiphilic oligomers of pyrenes

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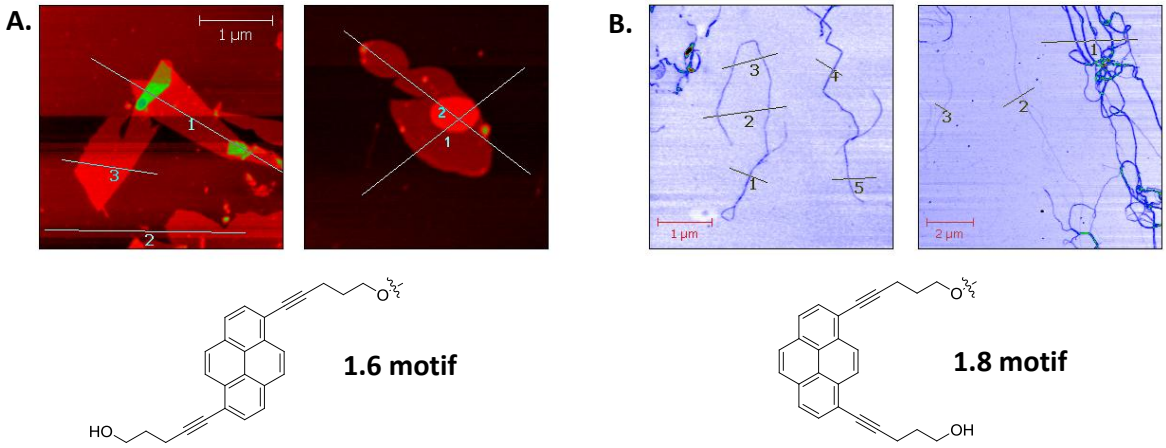
Very important aspects of the modern nanotechnology are control and prediction of arraying patterns of opto- and electroactive molecules in discrete objects on nanoscale level both on surface and solution. Consequqntly, a self-assembly of small molucules provides such an opportunity.[1] For example, oligopyrenotides (OPs, short amphiphilic pyrene oligomers) represent a novel class of amphiphilic molecules which tend to aggegate in aqueous phase.[2] As has been already shown, OPs are able to form 1D supramolecular polymer only under high salt concentration[3]. Since programmed arraying of polyaromatic hydrocarbons in structurally defined objects could offer enhanced performance over the individual components, prediction and controlling of their spatial arrangement remains challenging.

Herein we demonstrate that substitution type of the pyrene is crutial, and it determines a morphology of the assemblies. Thus, a 1.6-linkage causes a formation of large, free-standing 2D supromolecular polymers with a thickness 2 nm.[3] These assemblies possess a high degree of an internal order: the interior consists of hydrophobic pyrenes and alkyl chains, whereas the exterior exists as a net of hydrophilic negatively charged phosphates. Contrary, a 1.8-linkage exclusiveley leads to a formation of long (up to a few micrometer), nanometer thick helical supramolecular polymers. These structures tend to form even more complex structures (bundles, superhelixes). Moreover for both molecules, the polymerizations occurs via a nucleation-elongation mechanism. To study Py_3 self-assembly, we carried out whole set of spectroscopic (UV/vis, fluorescence, DLS) and microscopic experiments (AFM).



A. AFM images of 2D supramolecular polymers B. AFM images of the rod-like self-assembled molecules.

[1] Meijer, E. W.; Tom de Greef , F. A. *Nature* **2008**, *453*, 171-173
[2] Vybornyi, M.; Rudnev, A.; Langenegger, S.M.; Wandlowski,T.; Calzaferri, G.; Häner,R. *Angew. Chem. Int. Ed.* **2013**, *52*, 11488–11493.
[3] Nussbaumer, A. L.; Studer, D.; Malinovskii, V. L.; Häner, R. *Angew. Chem. Int. Ed.* **2011**, *50*, 5490–5494.